

06/11/99  
Jc672 U.S. PTO

Practitioner's Docket No. 50369

PATENT

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Box Patent Application  
Assistant Commissioner for Patents  
Washington, D.C. 20231

Jc525 U.S. PTO  
09/330417  
06/11/99

NEW APPLICATION TRANSMITTAL

Transmitted herewith for filing is the patent application of

Inventor(s): **Edward K. Pavelchek**

**WARNING:** 37 C.F.R. § 1.41(a)(1) points out:

"(a) A patent is applied for in the name or names of the actual inventor or inventors.

"(1) The inventorship of a nonprovisional application is that inventorship set forth in the oath or declaration as prescribed by § 1.63, except as provided for in § 1.53(d)(4) and § 1.63(d). If an oath or declaration as prescribed by § 1.63 is not filed during the pendency of a nonprovisional application, the inventorship is that inventorship set forth in the application papers filed pursuant to § 1.53(b), unless a petition under this paragraph accompanied by the fee set forth in § 1.17(i) is filed supplying or changing the name or names of the inventor or inventors."

For (title):

**ANTIREFLECTIVE HARD MASK COMPOSITIONS**

**CERTIFICATION UNDER 37 C.F.R. § 1.10\***

(Express Mail label number is mandatory.)

(Express Mail certification is optional.)

I hereby certify that this New Application Transmittal and the documents referred to as attached therein are being deposited with the United States Postal Service on this date June 11, 1999, in an envelope as "Express Mail Post Office to Addressee," mailing Label Number EJ704067435US, addressed to the: Assistant Commissioner for Patents, Washington, D.C. 20231.

Deanna M. Landry

(type or print name of person mailing paper)

Deanna M. Landry  
Signature of person mailing paper

**WARNING:** Certificate of mailing (first class) or facsimile transmission procedures of 37 C.F.R. § 1.8 cannot be used to obtain a date of mailing or transmission for this correspondence.

**\*WARNING:** Each paper or fee filed by "Express Mail" **must** have the number of the "Express Mail" mailing label placed thereon prior to mailing. 37 C.F.R. § 1.10(b).

"Since the filing of correspondence under § 1.10 without the Express Mail mailing label thereon is an oversight that can be avoided by the exercise of reasonable care, requests for waiver of this requirement will **not** be granted on petition." Notice of Oct. 24, 1996, 60 Fed. Reg. 56,439, at 56,442.

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## 1. Type of Application

This new application is for a(n)

(check one applicable item below)

- ☒ Original (nonprovisional)
- ☐ Design
- ☐ Plant

**WARNING:** Do not use this transmittal for a completion in the U.S. of an International Application under 35 U.S.C. § 371(c)(4), unless the International Application is being filed as a divisional, continuation or continuation-in-part application.

**WARNING:** Do not use this transmittal for the filing of a provisional application.

**NOTE:** If one of the following 3 items apply, then complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF A PRIOR U.S. APPLICATION CLAIMED and a NOTIFICATION IN PARENT APPLICATION OF THE FILING OF THIS CONTINUATION APPLICATION.

- ☐ Divisional.
- ☐ Continuation.
- ☐ Continuation-in-part (C-I-P).

## 2. Benefit of Prior U.S. Application(s) (35 U.S.C. §§ 119(e), 120, or 121)

**NOTE:** A nonprovisional application may claim an invention disclosed in one or more prior filed copending nonprovisional applications or copending international applications designating the United States of America. In order for a nonprovisional application to claim the benefit of a prior filed copending nonprovisional application or copending international application designating the United States of America, each prior application must name as an inventor at least one inventor named in the later filed nonprovisional application and disclose the named inventor's invention claimed in at least one claim of the later filed nonprovisional application in the manner provided by the first paragraph of 35 U.S.C. § 112. Each prior application must also be:

(i) An international application entitled to a filing date in accordance with PCT Article 11 and designating the United States of America; or

(ii) Complete as set forth in § 1.51(b); or

(iii) Entitled to a filing date as set forth in § 1.53(b) or § 1.53(d) and include the basic filing fee set forth in § 1.16; or

(iv) Entitled to a filing date as set forth in § 1.53(b) and have paid therein the processing and retention fee set forth in § 1.21(f) within the time period set forth in § 1.53(f).

37 C.F.R. § 1.78(a)(1).

**NOTE:** If the new application being transmitted is a divisional, continuation or a continuation-in-part of a parent case, or where the parent case is an International Application which designated the U.S., or benefit of a prior provisional application is claimed, then check the following item and complete and attach ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

**WARNING:** If an application claims the benefit of the filing date of an earlier filed application under 35 U.S.C. §§ 120, 121 or 365(c), the 20-year term of that application will be based upon the filing date of the earliest U.S. application that the application makes reference to under 35 U.S.C. §§ 120, 121 or 365(c). (35 U.S.C. § 154(a)(2) does not take into account, for the determination of the patent term, any application on which priority is claimed under 35 U.S.C. §§ 119, 365(a) or 365(b).) For a c-i-p application, applicant should review whether any claim in the patent that will issue is supported by an earlier application and, if not, the applicant should consider canceling the reference to the earlier filed application. The term of a patent is not based on a claim-by-claim approach. See Notice of April 14, 1995, 60 Fed. Reg. 20,195, at 20,205.

**WARNING:** When the last day of pendency of a provisional application falls on a Saturday, Sunday, or Federal holiday within the District of Columbia, any nonprovisional application claiming benefit of the provisional application **must** be filed prior to the Saturday, Sunday, or Federal holiday within the District of Columbia. See 37 C.F.R. § 1.78(a)(3).

- ☐ The new application being transmitted claims the benefit of prior U.S. application(s). Enclosed are ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

### 3. Papers Enclosed

A. Required for filing date under 37 C.F.R. § 1.53(b) (Regular) or 37 C.F.R. § 1.153 (Design) Application

19 Pages of specification

4 Pages of claims

1 Sheets of drawing

**WARNING:** **DO NOT** submit original drawings. A high quality copy of the drawings should be supplied when filing a patent application. The drawings that are submitted to the Office must be on strong, white, smooth, and non-shiny paper and meet the standards according to § 1.84. If corrections to the drawings are necessary, they should be made to the original drawing and a high-quality copy of the corrected original drawing then submitted to the Office. Only one copy is required or desired. For comments on proposed then-new 37 C.F.R. § 1.84, see Notice of March 9, 1988 (1990 O.G. 57-62).

**NOTE:** "Identifying indicia, if provided, should include the application number or the title of the invention, inventor's name, docket number (if any), and the name and telephone number of a person to call if the Office is unable to match the drawings to the proper application. This information should be placed on the back of each sheet of drawing a minimum distance of 1.5 cm. (5/8 inch) down from the top of the page . . ." 37 C.F.R. § 1.84(c)).

(complete the following, if applicable)

- ☐ The enclosed drawing(s) are photograph(s), and there is also attached a "PETITION TO ACCEPT PHOTOGRAPH(S) AS DRAWING(S)." 37 C.F.R. § 1.84(b).
- ☐ formal
- ☐ informal

B. Other Papers Enclosed

       Pages of declaration and power of attorney

1 Pages of abstract

       Other

### 4. Additional papers enclosed

- ☐ Amendment to claims
- ☐ Cancel in this applications claims \_\_\_\_\_ before calculating the filing fee. (At least one original independent claim must be retained for filing purposes.)
- ☐ Add the claims shown on the attached amendment. (Claims added have been numbered consecutively following the highest numbered original claims.)
- ☐ Preliminary Amendment
- ☐ Information Disclosure Statement (37 C.F.R. § 1.98)
- ☐ Form PTO-1449 (PTO/SB/08A and 08B)
- ☐ Citations

- ☐ Declaration of Biological Deposit
- ☐ Submission of "Sequence Listing," computer readable copy and/or amendment pertaining thereto for biotechnology invention containing nucleotide and/or amino acid sequence.
- ☐ Authorization of Attorney(s) to Accept and Follow Instructions from Representative
- ☐ Special Comments
- ☐ Other

**5. Declaration or oath (including power of attorney)**

*NOTE: A newly executed declaration is not required in a continuation or divisional application provided that the prior nonprovisional application contained a declaration as required, the application being filed is by all or fewer than all the inventors named in the prior application, there is no new matter in the application being filed, and a copy of the executed declaration filed in the prior application (showing the signature or an indication thereon that it was signed) is submitted. The copy must be accompanied by a statement requesting deletion of the names of person(s) who are not inventors of the application being filed. If the declaration in the prior application was filed under § 1.47, then a copy of that declaration must be filed accompanied by a copy of the decision granting § 1.47 status or, if a nonsigning person under § 1.47 has subsequently joined in a prior application, then a copy of the subsequently executed declaration must be filed. See 37 C.F.R. §§ 1.63(d)(1)–(3).*

*NOTE: A declaration filed to complete an application must be executed, identify the specification to which it is directed, identify each inventor by full name including family name and at least one given name, without abbreviation together with any other given name or initial, and the residence, post office address and country or citizenship of each inventor, and state whether the inventor is a sole or joint inventor. 37 C.F.R. § 1.63(a)(1)–(4).*

- ☐ Enclosed

Executed by

*(check all applicable boxes)*

- ☐ inventor(s).
- ☐ legal representative of inventor(s).  
37 C.F.R. §§ 1.42 or 1.43.
- ☐ joint inventor or person showing a proprietary interest on behalf of inventor who refused to sign or cannot be reached.
  - ☐ This is the petition required by 37 C.F.R. § 1.47 and the statement required by 37 C.F.R. § 1.47 is also attached. See item 13 below for fee.

- ☒ Not Enclosed.

*NOTE: Where the filing is a completion in the U.S. of an International Application or where the completion of the U.S. application contains subject matter in addition to the International Application, the application may be treated as a continuation or continuation-in-part, as the case may be, utilizing ADDED PAGE FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION CLAIMED.*

- ☐ Application is made by a person authorized under 37 C.F.R. § 1.41(c) on behalf of all the above named inventor(s).

*(The declaration or oath, along with the surcharge required by 37 C.F.R. § 1.16(e) can be filed subsequently).*

- ☐ Showing that the filing is authorized.  
*(not required unless called into question. 37 C.F.R. § 1.41(d))*

## 6. Inventorship Statement

**WARNING:** If the named inventors are each not the inventors of all the claims an explanation, including the ownership of the various claims at the time the last claimed invention was made, should be submitted.

The inventorship for all the claims in this application are:

☐ The same.

or

☐ Not the same. An explanation, including the ownership of the various claims at the time the last claimed invention was made,

☐ is submitted.

☐ will be submitted.

## 7. Language

**NOTE:** An application including a signed oath or declaration may be filed in a language other than English. An English translation of the non-English language application and the processing fee of \$130.00 required by 37 C.F.R. § 1.17(k) is required to be filed with the application, or within such time as may be set by the Office. 37 C.F.R. § 1.52(d).

☒ English

☐ Non-English

☐ The attached translation includes a statement that the translation is accurate. 37 C.F.R. § 1.52(d).

## 8. Assignment

☒ An assignment of the invention to Shipley Company, L.L.C. of  
Marlborough, Massachusetts

☐ is attached. A separate ☐ "COVER SHEET FOR ASSIGNMENT (DOCUMENT) ACCOMPANYING NEW PATENT APPLICATION" or ☐ FORM PTO 1595 is also attached.

☒ will follow.

**NOTE:** "If an assignment is submitted with a new application, send two separate letters—one for the application and one for the assignment." Notice of May 4, 1990 (1114 O.G. 77-78).

**WARNING:** A newly executed "CERTIFICATE UNDER 37 C.F.R. § 3.73(b)" must be filed when a continuation-in-part application is filed by an assignee. Notice of April 30, 1993, 1150 O.G. 62-64.

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## 9. Certified Copy

Certified copy(ies) of application(s)

Country	Appln. No.	Filed
Country	Appln. No.	Filed
Country	Appln. No.	Filed

from which priority is claimed

☐ is (are) attached.

☐ will follow.

NOTE: The foreign application forming the basis for the claim for priority must be referred to in the oath or declaration. 37 C.F.R. § 1.55(a) and 1.63.

NOTE: This item is for any foreign priority for which the application being filed directly relates. If any parent U.S. application or International Application from which this application claims benefit under 35 U.S.C. § 120 is itself entitled to priority from a prior foreign application, then complete item 18 on the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED.

## 10. Fee Calculation (37 C.F.R. § 1.16)

A. ☒ Regular application

CLAIMS AS FILED				
Number filed	Number Extra	Rate	Basic Fee	37 C.F.R. 1.16(a)
				\$760.00
Total				
Claims (37 C.F.R. § 1.16(c))	23 - 20 = 3	×	\$ 18.00	54.00
Independent				
Claims (37 C.F.R. § 1.16(b))	5 - 3 = 2	×	\$ 78.00	156.00
Multiple dependent claim(s),				
if any (37 C.F.R. § 1.16(d))		+	\$260.00	

☐ Amendment cancelling extra claims is enclosed.

☐ Amendment deleting multiple-dependencies is enclosed.

☐ Fee for extra claims is not being paid at this time.

NOTE: If the fees for extra claims are not paid on filing they must be paid or the claims cancelled by amendment, prior to the expiration of the time period set for response by the Patent and Trademark Office in any notice of fee deficiency. 37 C.F.R. § 1.16(d).

Filing Fee Calculation \$ 970.00

B. ☐ Design application  
(\$310.00—37 C.F.R. § 1.16(f))

Filing Fee Calculation \$

C. ☐ Plant application  
(\$480.00—37 C.F.R. § 1.16(g))

Filing fee calculation \$

## 11. Small Entity Statement(s)

- ☐ Statement(s) that this is a filing by a small entity under 37 C.F.R. § 1.9 and 1.27 is (are) attached.

**WARNING:** "Status as a small entity must be specifically established in each application or patent in which the status is available and desired. Status as a small entity in one application or patent does not affect any other application or patent, including applications or patents which are directly or indirectly dependent upon the application or patent in which the status has been established. The refiling of an application under § 1.53 as a continuation, division, or continuation-in-part (including a continued prosecution application under § 1.53(d)), or the filing of a reissue application requires a new determination as to continued entitlement to small entity status for the continuing or reissue application. A nonprovisional application claiming benefit under 35 U.S.C. § 119(e), 120, 121, or 365(c) of a prior application, or a reissue application may rely on a statement filed in the prior application or in the patent if the nonprovisional application or the reissue application includes a reference to the statement in the prior application or in the patent or includes a copy of the statement in the prior application or in the patent and status as a small entity is still proper and desired. The payment of the small entity basic statutory filing fee will be treated as such a reference for purposes of this section." 37 C.F.R. § 1.28(a)(2).

**WARNING:** "Small entity status must not be established when the person or persons signing the . . . statement can **unequivocally** make the required self-certification." M.P.E.P., § 509.03, 6th ed., rev. 2, July 1996 (emphasis added).

(complete the following, if applicable)

- ☐ Status as a small entity was claimed in prior application  
\_\_\_\_\_ / \_\_\_\_\_, filed on \_\_\_\_\_, from which benefit  
is being claimed for this application under:

35 U.S.C. § ☐ 119(e),  
☐ 120,  
☐ 121,  
☐ 365(c),

and which status as a small entity is still proper and desired.

- ☐ A copy of the statement in the prior application is included.

Filing Fee Calculation (50% of **A**, **B** or **C** above)

\$ \_\_\_\_\_

**NOTE:** Any excess of the full fee paid will be refunded if small entity status is established and a refund request are filed within 2 months of the date of timely payment of a full fee. The two-month period is not extendable under § 1.136. 37 C.F.R. § 1.28(a).

## 12. Request for International-Type Search (37 C.F.R. § 1.104(d))

(complete, if applicable)

- ☐ Please prepare an international-type search report for this application at the time when national examination on the merits takes place.

**13. Fee Payment Being Made at This Time**

☒ Not Enclosed

☒ No filing fee is to be paid at this time.

*(This and the surcharge required by 37 C.F.R. § 1.16(e) can be paid subsequently.)*

☐ Enclosed

☐ Filing fee \$ \_\_\_\_\_

☐ Recording assignment  
(\$40.00; 37 C.F.R. § 1.21(h))  
(See attached "COVER SHEET FOR  
ASSIGNMENT ACCOMPANYING NEW  
APPLICATION".) \$ \_\_\_\_\_

☐ Petition fee for filing by other than all the  
inventors or person on behalf of the inventor  
where inventor refused to sign or cannot be  
reached  
(\$130.00; 37 C.F.R. §§ 1.47 and 1.17(i)) \$ \_\_\_\_\_

☐ For processing an application with a  
specification in  
a non-English language  
(\$130.00; 37 C.F.R. §§ 1.52(d) and 1.17(k)) \$ \_\_\_\_\_

☐ Processing and retention fee  
(\$130.00; 37 C.F.R. §§ 1.53(d) and 1.21(l)) \$ \_\_\_\_\_

☐ Fee for international-type search report  
(\$40.00; 37 C.F.R. § 1.21(e)) \$ \_\_\_\_\_

NOTE: 37 C.F.R. § 1.21(l) establishes a fee for processing and retaining any application that is abandoned for failing to complete the application pursuant to 37 C.F.R. § 1.53(f) and this, as well as the changes to 37 C.F.R. §§ 1.53 and 1.78(a)(1), indicate that in order to obtain the benefit of a prior U.S. application, either the basic filing fee must be paid, or the processing and retention fee of § 1.21(l) must be paid, within 1 year from notification under § 53(f).

Total fees enclosed \$ \_\_\_\_\_

**14. Method of Payment of Fees**

☐ Check in the amount of \$ \_\_\_\_\_

☐ Charge Account No. \_\_\_\_\_ in the amount of \$ \_\_\_\_\_

A duplicate of this transmittal is attached.

NOTE: Fees should be itemized in such a manner that it is clear for which purpose the fees are paid. 37 C.F.R. § 1.22(b).



## 15. Authorization to Charge Additional Fees

**WARNING:** If no fees are to be paid on filing, the following items should not be completed.

**WARNING:** Accurately count claims, especially multiple dependent claims, to avoid unexpected high charges, if extra claim charges are authorized.

- ☐ The Commissioner is hereby authorized to charge the following additional fees by this paper and during the entire pendency of this application to Account No. \_\_\_\_\_:

- ☐ 37 C.F.R. § 1.16(a), (f) or (g) (filing fees)  
☐ 37 C.F.R. § 1.16(b), (c) and (d) (presentation of extra claims)

**NOTE:** Because additional fees for excess or multiple dependent claims not paid on filing or on later presentation must only be paid or these claims cancelled by amendment prior to the expiration of the time period set for response by the PTO in any notice of fee deficiency (37 C.F.R. § 1.16(d)), it might be best not to authorize the PTO to charge additional claim fees, except possibly when dealing with amendments after final action.

- ☐ 37 C.F.R. § 1.16(e) (surcharge for filing the basic filing fee and/or declaration on a date later than the filing date of the application)  
☐ 37 C.F.R. § 1.17(a)(1)–(5) (extension fees pursuant to § 1.136(a)).  
☐ 37 C.F.R. § 1.17 (application processing fees)

**NOTE:** “. . . A written request may be submitted in an application that is an authorization to treat any concurrent or future reply, requiring a petition for an extension of time under this paragraph for its timely submission, as incorporating a petition for extension of time for the appropriate length of time. An authorization to charge all required fees, fees under § 1.17, or all required extension of time fees will be treated as a constructive petition for an extension of time in any concurrent or future reply requiring a petition for an extension of time under this paragraph for its timely submission. Submission of the fee set forth in § 1.17(a) will also be treated as a constructive petition for an extension of time in any concurrent reply requiring a petition for an extension of time under this paragraph for its timely submission.” 37 C.F.R. § 1.136(a)(3).

- ☐ 37 C.F.R. § 1.18 (issue fee at or before mailing of Notice of Allowance, pursuant to 37 C.F.R. § 1.311(b))

**NOTE:** Where an authorization to charge the issue fee to a deposit account has been filed before the mailing of a Notice of Allowance, the issue fee will be automatically charged to the deposit account at the time of mailing the notice of allowance. 37 C.F.R. § 1.311(b).

**NOTE:** 37 C.F.R. § 1.28(b) requires “Notification of any change in status resulting in loss of entitlement to small entity status must be filed in the application . . . prior to paying, or at the time of paying, . . . the issue fee. . . .” From the wording of 37 C.F.R. § 1.28(b), (a) notification of change of status must be made even if the fee is paid as “other than a small entity” and (b) no notification is required if the change is to another small entity.

**16. Instructions as to Overpayment**

*NOTE: "... Amounts of twenty-five dollars or less will not be returned unless specifically requested within a reasonable time, nor will the payer be notified of such amounts; amounts over twenty-five dollars may be returned by check or, if requested, by credit to a deposit account." 37 C.F.R. § 1.26(a).*

- ☐ Credit Account No. \_\_\_\_\_
- ☐ Refund

65 F. B. I. 4-74

Reg. No. 33,860

Tel. No. (508) 485-7772

Customer No.



**SIGNATURE OF PRACTITIONER**

**Peter F. Corless**

*(type or print name of attorney)*

**P.O. Box 556**

P.O. Address

**Marlborough, MA 01752**

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☐ **Incorporation by reference of added pages**

*(check the following item if the application in this transmittal claims the benefit of prior U.S. application(s) (including an international application entering the U.S. stage as a continuation, divisional or C-I-P application) and complete and attach the ADDED PAGES FOR NEW APPLICATION TRANSMITTAL WHERE BENEFIT OF PRIOR U.S. APPLICATION(S) CLAIMED)*

- ☐ Plus Added Pages for New Application Transmittal Where Benefit of Prior U.S. Application(s) Claimed

Number of pages added \_\_\_\_\_

- ☐ Plus Added Pages for Papers Referred to in Item 4 Above

Number of pages added \_\_\_\_\_

- ☐ Plus added pages deleting names of inventor(s) named in prior application(s) who is/are no longer inventor(s) of the subject matter claimed in this application.

Number of pages added \_\_\_\_\_

- ☐ Plus "Assignment Cover Letter Accompanying New Application"

Number of pages added \_\_\_\_\_

☒ **Statement Where No Further Pages Added**

*(if no further pages form a part of this Transmittal, then end this Transmittal with this page and check the following item)*

- ☒ This transmittal ends with this page.

## ANTIREFLECTIVE HARD MASK COMPOSITIONS

### BACKGROUND OF THE INVENTION

#### 1. Field of the Invention

The present invention relates to compositions and methods for manufacture of integrated circuit systems. More particularly, organic spin-on type antireflective  
5 coating (ARC) compositions are provided that can exhibit good resistance to oxygen-based plasma etches and serve as hard masks in circuit manufacturing processes.

#### 2. Background

In the manufacture of semiconductor devices, a variety of conductive device  
10 regions and layers are formed on the device substrate, generally segregated by electrically insulating dielectric regions. Those dielectric regions may be formed e.g. from silicon dioxide and produced by various techniques, e.g. oxide growth, sputtering or other chemical deposition procedures. In the manufacture of the device, it is  
15 necessary to make openings in the dielectric layers to permit contact and electrical communication between different regions of the device.

Photolithography is employed to form such apertures in dielectric layers. A photoresist is patterned over the dielectric layer and the dielectric regions bared upon exposure are removed by a dry etch, typically a plasma etch or ion bombardment. See  
20 generally U.S. Patents 5,468,342 and 5,346,586.

However, resist mask also may degrade during the plasma etch of the underlying dielectric material, reducing resolution of the image patterned into the dielectric layer. Such imperfect image transfer can only compromise performance of  
25 the semiconductor device.

Certain inorganic materials known as hard masks have been interposed between dielectric and resist layers to reduce imperfections in image transfer from the resist

layer to the underlying dielectric layer. The hard mask material, e.g. polysilicon, silicon nitride, aluminum, titanium silicide, or tungsten, is vapor deposited such as by sputtering onto the dielectric layer. A photoresist is then coated and imaged over the hard mask. The inorganic hard mask regions bared upon resist development are removed by a plasma etch to which the organic resist layer is resistant. Relatively high etch selectivity can be achieved between the inorganic hard mask layer and the overcoated patterned organic-based resist. Such etch selectivity is generally not possible between a dielectric layer and an organic-based resist. Upon such etching, the hard mask profile matches the resist mask. Dielectric regions exposed upon hard mask etching now can be removed by an etch that is selective for the dielectric and for which the hard mask is resistant. Because high etch selectivity can be realized between the dielectric layer material and the hard mask, image transfer imperfections as discussed above can be avoided. See generally the above cited U.S. patents.

While such an approach can be effective for the manufacture of many integrated circuits, industry demands continue produce even smaller features at higher resolution.

Indeed, other problems in circuit manufacture that can limit resolution and the ability to form ever smaller features. For instance, reflection of activating radiation used to expose a photoresist can limit resolution of the image patterned in the resist. In particular, reflection of radiation from the underlying surface/photoresist interface can produce spatial variations in the radiation intensity in the photoresist, resulting in non-uniform photoresist linewidth upon development. Exposure radiation also can scatter from the underlying surface/photoresist interface into regions of the photoresist coating where exposure is not intended, again resulting in linewidth variation.

It thus would be desirable to have new compositions and methods for integrated circuit manufacture.

## SUMMARY OF THE INVENTION

The present invention provides new organic-based radiation absorbing compositions suitable for use as an antireflective coating composition ("ARC") for an overcoated photoresist.

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The antireflective compositions of the invention also can serve effectively as a hard mask layer by exhibiting a sufficient plasma etch selectively to an undercoated dielectric layer (e.g. an inorganic oxide or an organic layer) and an overcoated photoresist. The antireflective hard mask compositions of the invention contain a component that has inorganic substitution that can provide etch selectivity. For instance, preferred antireflective hard mask compositions of the invention include one or more components that comprises one or more inorganic elements, typically a member of Group IIIa, IVa, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, IVb and/or Vb of the Periodic Table, more preferably silicon, germanium, aluminum, particularly. For example, an antireflective hard mask composition of the invention can contain an organosilicon polymer, e.g. a copolymer provided by reaction of acrylate monomers that have Si substitution.

Antireflective hard mask compositions of the invention also preferably contain a chromophore component that can effectively absorb exposure radiation used to pattern an overlying resist layer. The chromophore can vary with the exposure wavelength employed for the overcoated photoresist. For instance, for a resist imaged at 248 nm, the antireflective hard mask composition may suitably contain a resin or other component that has anthracene or naphthyl groups. For a resist imaged at 193 nm, the antireflective hard mask composition may suitably contain a resin or other component that has phenyl groups. A single resin also may contain the radiation absorbing chromophore and inorganic groups that can provide etch selectivity. The antireflective hard compositions preferably are cured and crosslinked during processing.

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The invention also includes methods for patterning and treating a substrate, particularly an electronic packaging device such as a semiconductor wafer and the like.

More particularly, a preferred method of the invention includes providing a  
5 substrate (e.g. a semiconductor wafer) having a dielectric surface layer and applying a coating layer of an antireflective hard mask composition of the invention thereon. The organic antireflective hard mask composition can be applied by spin-coating, clearly more convenient than the typical vapor deposition employed for application of current inorganic hard mask layers.

10

A photoresist layer is then applied over the antireflective hard mask layer and the resist layer is imaged to patterned radiation and developed to provide a relief image over the antireflective layer. The antireflective hard mask is then etched with a plasma that is more reactive with the antireflective layer than the overcoated resist relief image,  
15 e.g. an etch selectively of antireflective hard mask layer:photoresist relief image of at least about 3:1, more preferably at least about 5:1, still more preferably at least about 7:1 or 10:1. For instance, an antireflective hard mask layer that contains a silicon inorganic component can be selectively etched with a fluorine-based plasma. An antireflective hard mask layer that contains an Al inorganic component can be  
20 selectively etched with a chlorine-based plasma.

That etch treatment provides a relief image of the antireflective hard mask composition that corresponds to that of the overlaying patterned resist. The bared dielectric layer areas are then etched with a plasma that is comparatively less reactive  
25 with the antireflective hard mask layer, e.g. an etch selectively of underlying dielectric layer:antireflective hard mask layer of at least about 3:1, more preferably at least about 5:1, still more about at least about 7:1 or 10:1. For instance, an Si-based dielectric layer such as a silicon nitride or silicon oxide layer could be selectively etched with a suitable halide plasma, and an organic dielectric layer could be selectively etched with  
30 an oxygen-based plasma. Substrate areas bared upon such etching of the dielectric

layer then can be selectively processed as desired, e.g. metallized.

To more specifically illustrate systems of the invention, an antireflective hard mask material that comprises Si can be etched with a halide plasma such as a fluorine or chlorine plasma, and an underlying organic dielectric layer can be selectively etched with an oxygen-based plasma. In another system, an antireflective hard mask material that comprises Al can be etched with a chlorine-based plasma, and an underlying SiO<sub>2</sub> dielectric layer can be selectively etched with a fluorine-based plasma.

The invention further provides novel articles of manufacture comprising substrates such as a microelectronic wafer coated with an antireflective hard mask composition of the invention alone or in combination with an overcoated photoresist composition and/or an underlying dielectric layer. Other aspects of the invention are disclosed *infra*.

#### BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 depicts schematically a preferred method of the invention.

#### DETAILED DESCRIPTION OF THE INVENTION

As discussed above, the invention provides novel antireflective hard mask compositions that can be applied as spin-on formulations. The compositions of the invention can exhibit good etch selectivity relative to an underlying dielectric layer, such as an inorganic material e.g. SiO<sub>2</sub> or other inorganic oxide, or an organic resin layer.

The antireflective hard mask compositions are mixtures of carbon groups and inorganic elements such as Si, As and/or Ge. References herein to inorganic atoms or elements are intended to refer to those non-carbon, multivalent elements other than hydrogen, nitrogen, oxygen or sulfur, preferably a member of Group IIb, IIIB, IVB, VB or VIB of the Periodic Table, more preferably a member of Group IIIB or IVB of the



Periodic Table.

5 An antireflective hard mask composition typically will contain at least 1 mole percent of inorganic elements, based on total solids (all components except solvent carrier) of the composition, more typically at least about 3 or 5 mole percent of inorganic elements, based on total solids (all components except solvent carrier) of the composition. More preferably, the antireflective hard mask composition will contain at least about 7, 10, 12 or 15 mole percent of inorganic elements based on total solids of the composition. Higher levels of inorganic content also will be suitable, e.g. where the  
10 antireflective hard mask composition contains at least about 17, 20, 25, 30, 35 or 40 mole percent of inorganic elements, based on total solids of the composition. The antireflective hard mask composition typically has a substantial carbon content, e.g. at least about 10, 15 or 20 mole percent of the composition based on total solids will be carbon. More preferably, at least about 25, 30, 35, 40, 50 or 60 mole percent of the  
15 composition based on total solids will be carbon. The one or more chromophores for absorbing exposure radiation of an overcoated photoresist typically will be aromatic carbon groups, as generally discussed above.

20 Referring now to the FIG. 1 of the drawings, where a particularly preferred method of the invention is generally depicted, in Step 1 a substrate 10 is provided having an overcoated dielectric layer 12. Substrate 10 may be e.g. an electronic packaging device such as a semiconductor wafer, microchip module and the like. For example, substrate 10 may be a silicon, silicon dioxide, aluminum or aluminum oxide microelectronic wafer. Other substrates that may be employed include gallium  
25 arsenide, gallium nitride, indium-based, ceramic, quartz or copper substrates.

Layer 12 may be an inorganic oxide e.g.  $\text{SiO}_2$ , resin layer such as parylene or a fluorinated amorphous carbon, or any of a variety of materials employed to segregate and electrically insulate features of the processed substrate 10.

In Step 2 of FIG. 1, a coating layer 14 of an organic antireflective hard mask composition of the invention is applied over layer 12. Coating layer 14 may be applied by spin coating a liquid coating formulation over layer 12, followed by removal of the solvent carrier such as by vacuum hotplate at about 90°C for 60 seconds. The antireflective hard mask composition in general is applied on a substrate with a dried layer thickness of between about 0.02 and 0.5  $\mu\text{m}$ , more typically a dried layer thickness of between about 0.04 and 0.20  $\mu\text{m}$ .

As discussed above, the antireflective hard mask composition coating contains a component that has chromophore moieties for absorption of exposure radiation of an overcoated photoresist layer as well as inorganic groups to provide plasma etch selectivity with respect to the underlying dielectric layer 12.

Preferred antireflective hard mask compositions of the invention include those that contain a resin that has chromophore and/or inorganic groups thereon. The resin is preferably organic. For instance, a polymer may be employed that has pendant chromophore groups, such as carbocyclic aryl or heteroaromatic groups for effective absorption of exposure radiation, e.g. anthracenyl (for 248 nm), phenyl (for 193 nm), naphthylene, and the like. Preferred chromophores and resins containing same are disclosed in U.S. Patent 5,851,730 and European Published Application 813114A2, both assigned to the Shipley Company.

A resin that has both chromophore and etch-resistant inorganic groups can be readily prepared by reaction of a mixture of appropriate monomers, e.g. reaction of a monomer incorporating an inorganic, etch resistant element (e.g. Si, Ge, Al and the like) together with a monomer that has a desired chromophore group. Such monomers are commercially available or can be readily synthesized. For instance, acrylate monomers that include Si groups are available from a number of commercial sources such as Gelest, Inc. (Tullytown, PA) and others. More particularly, exemplary monomers include methacryloxymethyltris-(trimethylsiloxy)silane,

allyltris(trimethylsiloxy)silane, allyltrimethoxysilane, vinyltris(trimethylsiloxy)silane, vinyltrimethoxysilane, vinyl(3,3,3-trifluoropropyl)dimethylsilane, vinyltriphenoxysilane, vinyltriethylsilane, vinyltriacetoxysilane, and the like. Vinyl-terminated silicon polymers also are available, such as vinyl terminated or  
5 methacryloxypropyl terminated p-dimethylsiloxane, which can be incorporated into other polymers by appropriate reaction, e.g. free radical polymerization in the presence of an initiator such as 2,2'-azobisisobutyronitrile, preferably in a suitable solvent such as tetrahydrofuran and the like, typically with heating until reaction completion. See  
10 Example 1 which follows for exemplary synthesis of an antireflective hard mask polymer of the invention.

In the same manner, other inorganic materials can be incorporated into components of an antireflective hard mask composition for use in accordance with the invention. For instance, other polymerizable monomers that have one or more desired  
15 inorganic atoms can be reacted to form a resin. Such monomers are commercially available from sources such as Gelest, Inc. and others. For example, suitable monomers may include allyltriethylgermane, allyltrimethylgermane, methacryloxytriethylgermane, tetrallylgermane, vinyltriethylgermane, and the like. Suitable aluminum materials also are commercially available.

20 Additionally, the inorganic etch-resistant component and antireflective component can be separate, blended materials of an antireflective hard mask composition of the invention. For instance, polymers with an inorganic content can be blended with organic polymers that contain the exposure radiation-absorbing  
25 chromophores. For instance, examples of suitable inorganic, etch-resistant polymers include silsesquioxanes such as p-methylsilsesquioxane which has a high silicon content and lesser silanol content; epoxypropoxypropyl terminated p-dimethylsiloxanes; carbinol functional copolymers of methylsiloxane and dimethylsiloxane; alcohol terminated copolymers of dimethylsiloxane and ethylene  
30 oxide; and silanol terminated p-dimethylsiloxane. Inorganic crosslinkers also could be

employed. For example, aluminum crosslinkers may be suitable to provide the desired inorganic content to an antireflective hard mask composition, such as aluminum s-butoxide bis(ethylacetoacetate). Exemplary organic-based polymers with chromophores that could be blended with such polymers are disclosed in Shipley's U.S. Patent  
5 5,851,730 and European Published Application 813114A2. For 193 nm resist imaging, suitable phenyl-containing polymers are disclosed in copending application 09/153,575, filed September 15, 1998, assigned to the Shipley Company. That application discloses *inter alia* a preferred antireflective terpolymer consisting of polymerized groups of styrene, 2-hydroxyethylmethacrylate and methylmethacrylate at  
10 a respective mole ratio of those groups of 30:38:32.

Polymers of antireflective hard mask compositions of the invention may contain other units in addition to inorganic, etch resistant elements and chromophore units. For instance, resins of compositions of the invention may have pendant cyano groups;  
15 itaconic anhydride groups; alicyclic groups such as adamantyl, norbornyl, cyclohexyl, etc.; carbocyclic aryl groups such as naphthyl, phenol; etc.

Preferably, the combined resin or oligomer components of an antireflective hard mask composition of the invention will have one or more inorganic, etch resistant  
20 elements present in an amount of at least about 3, 4, 5, 6, 7 or 8 mole percent of the total molar amount of resins or oligomers of the composition. Even higher content of inorganic, etch-resistant atoms may be employed, e.g. a concentration of inorganic, etch resistant elements of at least about 10, 12, 15, or 20 mole percent based on the total amount of resins or oligomers of the compositions. As discussed herein, typical  
25 components of an antireflective hard mask composition of the invention are the resin or oligomer components that contain the antireflective chromophore and inorganic, etch-resistant element; if a crosslinking composition, a crosslinker, typically with an acid source; and a solvent carrier. The compositions may however comprise additional components. For instance, the antireflective chromophore and inorganic, etch-resistant  
30 element may be provided by non-polymeric, small molecule (e.g. molecular weight less

than about 500) additives.

Molecular weights of resins of antireflective hard mask compositions of the invention can vary relatively widely, e.g. weight average molecular weight (Mw) of  
5 about 1,000 to about 1,000,000 daltons.

The concentration of the antireflective chromophore and inorganic, etch-resistant component(s) of compositions of the invention may vary within relatively broad ranges, and in general those component(s) are employed in a concentration of  
10 from about 50 to 95 weight percent of the total of the dry components of the composition, more typically from about 60 to 90 weight percent of the total dry components (all components except solvent carrier).

Crosslinking-type antireflective hard mask compositions of the invention also  
15 contain a crosslinker component or material. A variety of crosslinkers may be employed, including those ARC crosslinkers disclosed in the above-mentioned Shipley U.S. Patent 5,851,730, such as glycouril crosslinkers, particularly methoxy methylated glycouril commercially available under the tradename of Powderlink 1174 from the American Cyanamid Co. Other amine-based crosslinkers may be suitable. For  
20 example, melamine crosslinkers may be suitable, particularly melamine-formaldehyde resins such as those sold under the tradename Cymel by American Cyanamid such as Cymel 300, 301, 303, 350. Benzoguanamine-based resins and urea-based resins also may be suitable such as the urea resins sold as Bettel 60, 65 and 80 by American Cyanamid, and the benzoguanamine resins sold under the trade names of Cymel 1123  
25 and 1125 by American Cyanamid.

Crosslinking antireflective hard mask compositions of the invention preferably further comprise an acid or acid generator compound for catalyzing or promoting reaction of the crosslinker during curing of the antireflective hard mask coating layer.  
30 Preferably an acid generator compound is employed that liberates acid upon photolysis

or thermal treatment. Preferably the acid generator is a thermal acid generator is employed, i.e. a compound that generates acid upon thermal treatment. A variety of known thermal acid generators are suitably employed such as e.g. benzoin tosylate, nitrobenzyl tosylate particularly 4-nitrobenzyl tosylate, and other alkyl esters of organic sulfonic acids. A preferred thermal acid generator is Nacure 5225 available from King Industries. Compounds that generate a sulfonic acid upon activation are generally suitable. Typically a thermal acid generator is present in a crosslinking antireflective hard mask composition in concentration of from about 0.3 to 3 percent by weight of the total of the dry components of the composition. Instead of or in addition to a thermal acid generator, a photoacid generator may be employed as an acid generator, and the antireflective hard mask coating layer blanket exposed to activating radiation prior to application of an overcoated photoresist composition.

Also, rather than an acid generator, an acid may be simply formulated into a crosslinking antireflective hard mask composition of the invention, particularly for antireflective hard mask compositions that require heating to cure in the presence of acid so that the acid does not promote undesired reaction of composition components prior to use of the composition. Suitable acids include e.g. sulfonic acids such as toluene sulfonic acid and sulfonic acid, triflic acid, or mixtures of those materials.

The present invention also includes antireflective hard mask compositions that do not undergo significant cross-linking during intended use with a photoresist composition. Such non-crosslinking compositions need not include a crosslinker component or an acid or thermal acid generator for inducing or promoting a crosslinking reaction. In other words, such non-crosslinking antireflective hard mask compositions typically will be essentially free (i.e. less than about 1 or 2 weight percent) or completely free of a crosslinker component and/or acid source for promoting a crosslinking reaction.

Referring again to Step 2 of FIG. 1, if the antireflective hard mask composition

is a crosslinking-type composition, the composition is preferably at least partially cured at this step, prior to application of a photoresist layer. Thermal treatment is generally preferred. Cure or crosslinking conditions will vary with the components of the antireflective hard mask composition. Suitable conditions may include e.g. heating the coated substrate 10 at about 200°C for about 10 to 30 minutes.

Antireflective compositions of the invention preferably also comprise one or more photoacid generators (i.e. "PAG") that are suitably employed in an amount sufficient to inhibit or substantially prevent undesired notching or footing of an overcoated photoresist layer. In this aspect of the invention, the photoacid generator is not used as an acid source for promoting a crosslinking reaction, and thus preferably the photoacid generator is not substantially activated during crosslinking of the antireflective composition (in the case of a crosslinking antireflective hard mask). In particular, with respect to antireflective hard mask compositions that are thermally crosslinked, the antireflective hard mask composition PAG should be substantially stable to the conditions of the crosslinking reaction so that the PAG can be activated and generate acid during subsequent exposure of an overcoated resist layer. Specifically, preferred PAGs do not substantially decompose or otherwise degrade upon exposure of temperatures of from about 140°C or 150°C to 190°C for 5 to 30 or more minutes. Such PAGs and the use thereof in antireflective coating composition are disclosed in U.S. patent application serial number 08/797,741, filed February 6, 1997 of Pavelchek et al and corresponding Japanese Patent Application no. 10-61845, both assigned to the Shipley Company. Suitable PAGs for use in the antireflective hard mask compositions of the invention are identified in the below discussion of photoresist PAGs. Generally preferred photoacid generators for such use in ARCs of the invention include e.g. onium salts such as di(4-tert-butylphenyl)iodonium perfluorooctane sulphonate, and halogenated non-ionic photoacid generators such as 1,1-bis[p-chlorophenyl]-2,2,2-trichloroethane.

Antireflective hard mask compositions of the invention also may contain

additional dye compounds that absorb radiation used to expose an overcoated photoresist layer. Other optional additives include surface leveling agents, for example, the leveling agent available under the tradename Silwet 7604 from Union Carbide, or the surfactant FC 430 available from the 3M Company. Preferred  
5 surfactant is concentration between 0.2 to 1.5% of solids.

To make a liquid coating antireflective hard mask composition suitable for spin-on applications, the composition components are dissolved in a suitable solvent such as, for example, ethyl lactate or one or more of the glycol ethers such as 2-  
10 methoxyethyl ether (diglyme), ethylene glycol monomethyl ether, and propylene glycol monomethyl ether; solvents that have both ether and hydroxy moieties such as methoxy butanol, ethoxy butanol, methoxy propanol and ethoxy propanol; esters such as methyl cellosolve acetate, ethyl cellosolve acetate, propylene glycol monomethyl ether acetate, dipropylene glycol monomethyl ether acetate and other solvents such as dibasic esters,  
15 propylene carbonate and gamma-butyro lactone. The concentration of the dry components in the solvent will depend on several factors such as the method of application. In general, the solids content of an antireflective hard mask composition varies from about 0.5 to 20 weight percent of the total weight of the antireflective hard mask composition, preferably the solids content varies from about 2 to 10 weight  
20 percent of the total weight of the composition.

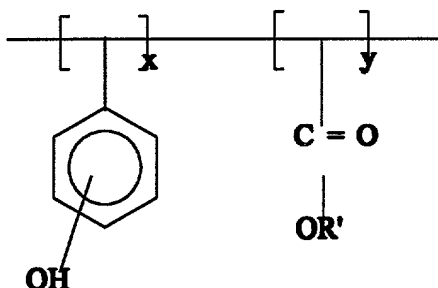
Referring now to Step 3 of FIG. 1, a photoresist coating layer 16 is applied over the antireflective hard mask layer 14. As with application of layer 14, the resist can be applied by any standard means such as spinning.

25

A variety of photoresist compositions can be employed with the antireflective hard mask compositions of the invention, including positive-acting and negative-acting photoacid-generating compositions. Photoresists for use with ARCs of the invention in general contain a resin binder and a photoactive component, typically a photoacid  
30 generator compound. Preferably the photoresist resin binder has functional groups that



impart alkaline aqueous developability to the imaged resist composition. Generally particularly preferred photoresists for use with antireflective compositions of the invention are positive-acting and negative-acting chemically-amplified resists. A number of chemically-amplified resist compositions have been described, e.g., in U.S. Patents Nos. 4,968,581; 4,883,740; 4,810,613; 4,491,628 and 5,492,793, all of which are incorporated herein by reference for their teaching of making and using chemically amplified positive-acting resists. A particularly preferred chemically amplified photoresist for use with an antireflective composition of the invention comprises in admixture a photoacid generator and a resin binder that comprises a copolymer containing both phenolic and non-phenolic units. For example, one preferred group of such copolymers has acid labile groups substantially, essentially or completely only on non-phenolic units of the copolymer. One especially preferred copolymer binder has repeating units x and y of the following formula:



wherein the hydroxyl group be present at either the ortho, meta or para positions throughout the copolymer, and R' is substituted or unsubstituted alkyl having 1 to about 18 carbon atoms, more typically 1 to about 6 to 8 carbon atoms. *Tert*-butyl is a generally preferred R' group. An R' group may be optionally substituted by e.g. one or more halogen (particularly F, Cl or Br), C<sub>1-8</sub> alkoxy, C<sub>2-8</sub> alkenyl, etc. The units x and y may be regularly alternating in the copolymer, or may be randomly interspersed through the polymer. Such copolymers can be readily formed. For example, for resins of the above formula, vinyl phenols and a substituted or unsubstituted alkyl acrylate such as *t*-butylacrylate and the like may be condensed under free radical conditions as known in the art. The substituted ester moiety, i.e. R'-O-C(=O)-, moiety of the acrylate

units serves as the acid labile groups of the resin and will undergo photoacid induced cleavage upon exposure of a coating layer of a photoresist containing the resin.

Preferably the copolymer will have a Mw of from about 8,000 to about 50,000, more preferably about 15,000 to about 30,000 with a molecular weight distribution of about 3 or less, more preferably a molecular weight distribution of about 2 or less. Non-phenolic resins, e.g. a copolymer of an alkyl acrylate such as *t*-butylacrylate or *t*-butylmethacrylate and a vinyl alicyclic such as a vinyl norbornyl or vinyl cyclohexanol compound, also may be used as a resin binder in compositions of the invention. Such copolymers also may be prepared by such free radical polymerization or other known procedures and suitably will have a Mw of from about 8,000 to about 50,000, and a molecular weight distribution of about 3 or less. Additional preferred chemically-amplified positive resists are disclosed in U.S. Patent 5,258,257 to Sinta et al.; U.S. Patent 5,700,624 to Thackeray et al.; and U.S. Patent 5,861,231 to Barclay et al.

Preferred negative-acting resist compositions for use with an antireflective composition of the invention comprise a mixture of materials that will cure, crosslink or harden upon exposure to acid, and a photoacid generator. Particularly preferred negative-acting resist compositions comprise a resin binder such as a phenolic resin, a crosslinker component and a photoactive component of the invention. Such compositions and the use thereof have been disclosed in European Patent Applications 0164248 and 0232972 and in U.S. Patent No. 5,128,232 to Thackeray et al. Preferred phenolic resins for use as the resin binder component include novolaks and poly(vinylphenol)s such as those discussed above. Preferred crosslinkers include amine-based materials, including melamine, glycourils, benzoguanamine-based materials and urea-based materials. Melamine-formaldehyde resins are generally most preferred. Such crosslinkers are commercially available, e.g. the melamine resins sold by American Cyanamid under the trade names Cymel 300, 301 and 303. Glycouril resins are sold by American Cyanamid under trade names Cymel 1170, 1171, 1172, Powderlink 1174, urea-based resins are sold under the trade names of Beetle 60, 65 and 80, and benzoguanamine resins are sold under the trade names Cymel 1123 and 1125.

Suitable photoacid generator compounds of resists used with antireflective hard mask compositions of the invention include the onium salts, such as those disclosed in U.S. Patent Nos. 4,442,197, 4,603,101, and 4,624,912, each incorporated herein by reference; and non-ionic organic photoactive compounds such as the halogenated  
5 photoactive compounds as in U.S. Patent 5,128,232 to Thackeray et al. and sulfonate photoacid generators including sulfonated esters and sulfonyloxy ketones. See *J. of Photopolymer Science and Technology*, 4(3):337-340 (1991), for disclosure of suitable sulfonate PAGS, including benzoin tosylate, t-butylphenyl alpha-(p-toluenesulfonyloxy)-acetate and t-butyl alpha-(p-toluenesulfonyloxy)-acetate.

10 Preferred sulfonate PAGs are also disclosed in U.S. Patent 5,344,742 to Sinta et al. The camphorsulfonate PAGs of formulae I and II at column 6 of U.S. Patent 5,879,856 are also preferred photoacid generators for resist compositions used with the antireflective compositions of the invention, particularly chemically-amplified resists of the invention.

15 In Step 3 of FIG. 1, after application of resist layer 16 as discussed above, the photoresist coating layer is typically dried by heating to remove solvent preferably until the resist layer is tack free. Optimally, essentially no intermixing of the ARC layer and photoresist layer should occur.

20 The resist layer is then imaged with activating radiation through a mask in conventional manner. The exposure energy is sufficient to effectively activate the photoactive component of the resist system to produce a patterned image in the resist coating layer, more specifically, the exposure energy typically ranges from about 3 to  
25 300 mJ/cm<sup>2</sup> depending upon the exposure tool. The exposed resist layer may be subjected to a post-exposure bake if desired to create or enhance solubility differences between exposed and unexposed regions of a coating layer. For example, negative acid-hardening photoresists typically require post-exposure heating to induce the acid-promoted crosslinking reaction, and many chemically amplified positive-acting resists  
30 require post-exposure heating to induce an acid-promoted deprotection reaction.

Typically post-exposure bake conditions include temperatures of about 50°C or greater, more specifically a temperature in the range of from about 50°C to 160°C. Resists can be imaged with a wide range of exposure energy, e.g. I-line radiation (365 nm), deep UV particularly 248 nm, sub-200 nm wavelengths such as 193 nm and 157 nm, e-  
5 beam, EUV, ion projection lithography (IPL) and extremely short wavelength exposure such as X-ray and other sub-20 nm imaging.

After the latent image is formed in the resist layer, in Step 4 of FIG. 1 the resist is developed (i.e. exposed areas removed in the case of a positive resist, unexposed  
10 areas removed in the case of a negative resist). Wet development will be suitable, e.g. with an aqueous tetrabutylammonium hydroxide solution, or other aqueous alkaline solution to provide resist relief images 16' over antireflective hard mask layer 14 as shown in Step 4 of FIG. 1. The photoresist layer also may be dry developed with a plasma (e.g. oxygen-based plasma) if desired.

15 In Step 5, antireflective hard mask layer 14 is patterned with a plasma distinct from the plasma employed to form the overlying resist relief images 16'. For instance, antireflective hard mask layer can be etched with a halide-based plasma such as a fluorine or chlorine-based plasma to provide antireflective hard mask relief images 14' that correspond to the overlying resist relief images 16' as shown in Step 5 of FIG. 1.  
20 A preferred material, particularly to etch an antireflective hard mask layer containing Si, is a plasma formed in a gas flow of CF<sub>3</sub>, preferably in the substantial (less than 3 or 5 molar %) absence of oxygen. A chlorine-based plasma etchant is particularly to etch an antireflective hard mask layer containing Al.

25 Thereafter, as shown in Step 6 of FIG. 1, the underlying dielectric layer 12 can be etched e.g. by an oxygen-based plasma which removes resist relief images 16' and dielectric layer 12 not masked by patterned antireflective hard mask layer 14', which is resistant to the oxygen-based plasma because of the inorganic component of that layer  
30 as discussed above.

The selectively defined surface of substrate 10 can then be processed as desired, e.g. the defined areas can be metallized such as by vapor deposited copper, aluminum, tungsten, or other conductive metal, or alloys thereof to provide circuit traces or electrical interconnect vias 19 as depicted in Step 7 of FIG. 1. A preferred metal to form vias or traces 19 is CVD copper, or electroplated copper.

All documents mentioned herein are incorporated herein by reference. The following non-limiting examples are illustrative of the invention.

Example 1: Synthesis of organosilicon polymer of the invention.

15.00 grams of 9-anthracenemethyl methacrylate, 5.61 grams of 2-hydroxyethyl methacrylate, and 26.33 grams of 3[tris(trimethylsilyloxy)silyl]propyl methacrylate were dissolved in 320 grams of tetrahydrofuran. The solution was degassed with a stream of dry nitrogen for 10 minutes and heated to 45°C. 0.475 grams of the polymerization initiator 2,2'azobisisobutyronitrile was then added to the solution and the solution heated at reflux for 24 hours. The polymer product was isolated by precipitation into 12 L of deionized water and dried in vacuum. Yield 84%. Weight average molecular weight (vs. polystyrene standards) 22,000.

Example 2: Preparation and use of a composition of the invention

An ARC/hard mask composition of the invention is prepared by admixing the following components: organosilicon polymer of Example 1 above (10 grams), Powderlink 1174 glycouril crosslinker (1.5 grams), para-toluenesulfonic acid (0.2 grams) in a solvent of ethyl lactate to provide a formulation at about 4 weight percent total solids.

That ARC/hard mask composition is spin coated onto a cured dielectric layer (epoxy layer) and dried to provide a coating layer thickness of about 100 nm. A commercially available positive photoresist is then spin coated over the ARC layer to a

5

The foregoing description of the invention is merely illustrative thereof, and it is understood that variations and modifications can be effected without departing from the scope or spirit of the invention as set forth in the following claims.

What is claimed is:

1. A method for etching a dielectric layer overlying an integrated circuit or electronic packaging substrate, comprising:
  - (a) providing an integrated circuit substrate having a dielectric layer thereon;
  - (b) over the dielectric layer, depositing coating layer of an organic antireflective hard mask composition that comprises one or more inorganic elements selected from Group IIIa, IVa, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, IVb or Vb of the Periodic Table;
  - (c) depositing a coating layer of a photoresist composition over the antireflective hard mask composition coating layer;
  - (d) exposing to patterned radiation and developing the photoresist composition coating layer to form to form a photoresist relief image over the antireflective hard mask composition;
  - (e) etching the antireflective hard mask composition to form a relief image thereof; and
  - (f) etching bared dielectric layer areas.
2. The method of claim 1 wherein the antireflective hard mask composition contains at least about 20 mole percent of carbon and at least about 1 mole percent of inorganic atoms, based on total solids of the composition.
3. The method of claim 1 wherein the antireflective hard mask composition has about 5 mole percent of inorganic atoms, based on total solids of the composition.
4. The method of claim 1 wherein the inorganic atoms of the antireflective hard mask composition are selected from the group consisting of Si, Al and Ge.

5. The method of claim 1 wherein the antireflective hard mask composition is deposited by spin coating.

6. The method of claim 1 wherein the antireflective hard mask composition comprises a component that has aromatic groups.

7. The method of claim 6 wherein the aromatic groups are carbocyclic aryl groups.

8. The method of claim 6 wherein the aromatic groups are optionally substituted anthracenyl groups, optionally substituted naphthyl groups or optionally substituted phenyl groups.

9. The method of claim 1 wherein the photoresist composition is imaged with radiation having a wavelength of about 248 nm, and the antireflective hard mask composition comprises a component that has optionally substituted anthracene groups or optionally substituted naphthyl groups.

10. The method of claim 1 wherein the photoresist composition is imaged with radiation having a wavelength of about 193 nm, and the antireflective hard mask composition comprises a component that has optionally substituted phenyl groups.

11. The method of claim 1 wherein the dielectric layer is etched with a plasma containing oxygen.

12. The method of claim 1 wherein the antireflective hard mask composition layer is etched with a halide plasma.

13. The method of claim 1 wherein the antireflective hard mask layer is at least about three times less reactive to an oxygen plasma etch than the dielectric layer.



14. The method of claim 1 wherein the antireflective hard mask composition comprises a thermal acid generator compound.

15. The method of claim 1 wherein the antireflective hard mask composition is thermally cured prior to applying the photoresist composition layer.

16. The method of claim 1 wherein the antireflective hard mask composition comprises a photoacid generator, and the photoacid generator is not substantially activated until the exposing of the photoresist composition layer.

17. The method of claim 1 wherein the antireflective hard mask composition comprises a crosslinker material.

18. A method for etching a dielectric layer overlying an integrated circuit or electronic packaging substrate, comprising:

- (a) providing a substrate having a dielectric layer thereon;
- (b) over the dielectric layer, depositing a coating layer of an organic antireflective hard mask composition that is at least about three times less reactive to an oxygen plasma etch than the dielectric layer;
- (c) depositing a coating layer of a photoresist composition over the antireflective hard mask composition coating layer;
- (d) exposing to patterned radiation and developing the photoresist composition coating layer to form a photoresist relief image over the antireflective hard mask composition;
- (e) etching the antireflective hard mask composition to form a relief image thereof; and
- (f) etching bared dielectric layer areas.

19. The method of claim 18 wherein the antireflective hard mask composition is at least about 5 times less reactive to an oxygen plasma than the dielectric composition layer.

20. The method of claim 19 wherein the antireflective hard mask layer is etched with a halide plasma.

21. A coated substrate comprising:  
a substrate having a dielectric layer thereon;  
over the dielectric layer, a coating layer of an organic antireflective hard mask composition that comprises one or more inorganic elements selected from Group IIIa, IVa, Va, VIa, VIIa, VIII, Ib, IIb, IIIb, IVb or Vb of the Periodic Table; and  
over the antireflective hard mask composition coating layer, a coating layer of a photoresist composition.

22. A coated substrate comprising:  
a substrate having a dielectric layer thereon;  
over the dielectric layer, a coating layer of an organic antireflective hard mask composition; and  
over the antireflective hard mask composition coating layer, a coating layer of a photoresist composition.

23. An antireflective hard mask composition for use with an overcoated photoresist layer, comprising:  
at least about 20 mole percent of carbon and at least about 1 mole percent of Si, Ge or Al atoms, based on total solids of the composition, and an organic chromophore that can absorb exposure radiation used to pattern the overlying photoresist layer.

# ABSTRACT OF THE DISCLOSURE

New organic-based radiation absorbing compositions are provided that are suitable for use as an antireflective coating composition ("ARC") for an overcoated photoresist. These compositions also serve effectively as a hard mask layer by exhibiting a sufficient plasma etch selectively from an undercoated dielectric layer.

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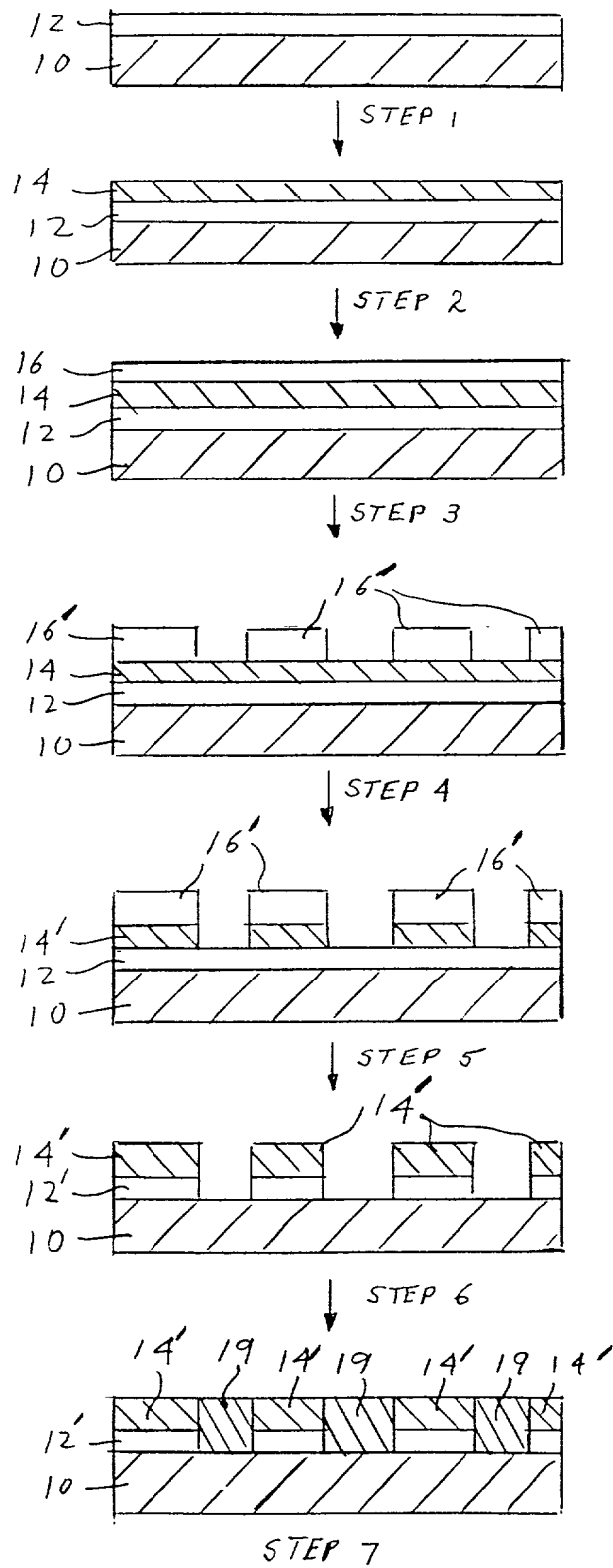


FIG. 1